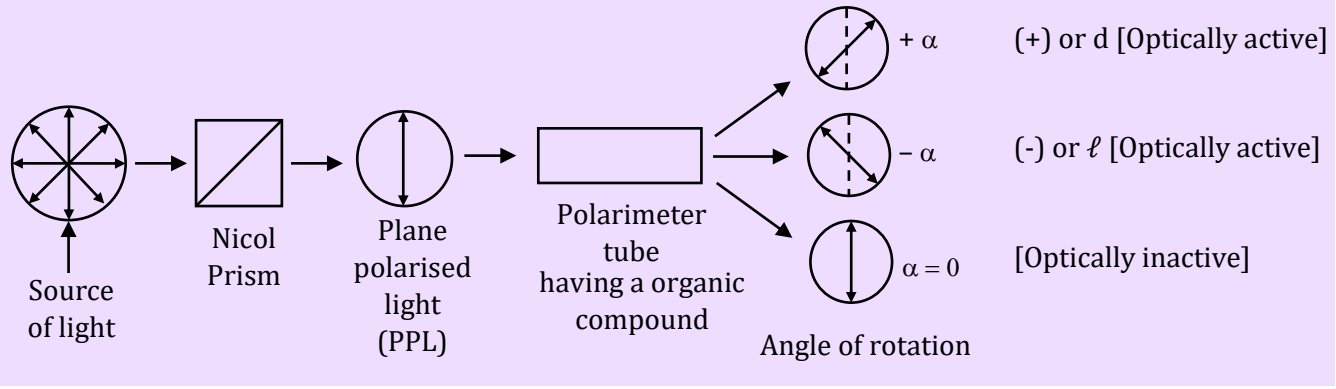
01 Optical Isomerism

Optical Isomerism

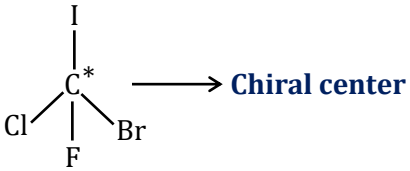
Two or more than two compounds have same molecular formula, same structural formula but different behaviour towards PPL (plane polarised light) are called optical isomers, and the phenomenon is called optical isomerism.



1. **Optical activity :** Tendancy to rotate plane of PPL in a particular direction. If a compound rotates plane of PPL in clockwise direction then it will be dextrorotatory or d or (+) and if a compound rotates plane of PPL in anticlockwise direction then it will be laevorotatory or ℓ or (–).
   - Clockwise rotation = dextrorotatory = 'd' or (+)
   - Anticlockwise rotation = laevorotatory = 'l' or (-)
   - Angle of rotation (α) depends on –

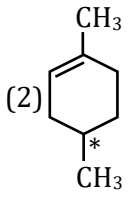
   (a) Concentration of solution (in gm/ml) **(b) Length of polarimeter tube (in dm)**
   (c) Wavelength of light used (in Å) **(d) Temperature (°C), etc.**

2. **Chiral Centre:** sp^3 hybridised atom [C, N, O, P, S] having four different valencies or four different atoms groups attached to it.



3. **Chiral carbon / asymmetric carbon:** sp^3 carbon atom attached with four different atoms or groups is known as chiral or asymmetric carbon it can be represented by :- Asterisk (*).

Ex. (1) $H_5C_2-\overset{*}{C}H(Me)-\overset{*}{C}H(Cl)-CH_2-CH_3$

(2) 

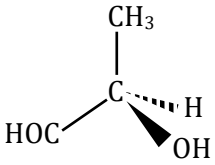
Representations of tetrahedral carbon

1. Wedge-dash OR 3–D representation
2. Fischer projection OR 2–D representation
3. Sawhorse projection
4. Newman projection

Wedge-Dash Formula (3D)

Out of 4 units, 2 units including tetrahedral carbon is maintained in the plane and remaining two units below and above the plane.

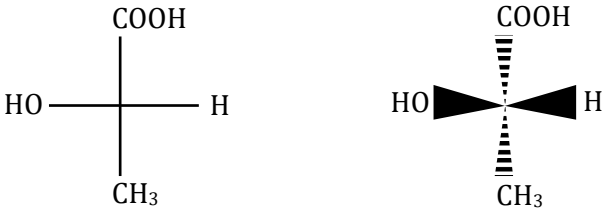
Example: CH_3—CH(OH)—COOH



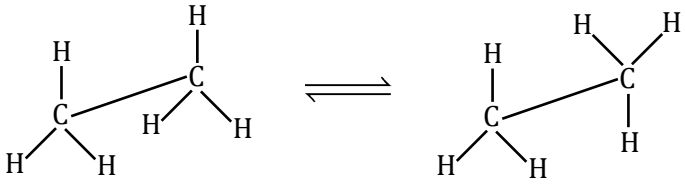
Fischer Projection (2-D)

Groups at horizontal line towards observer.

Groups at vertical line away from observer.



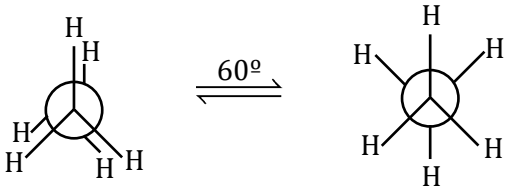
Saw horse projection



Eclipsed **Staggered**

Saw horse projection

Newman projection



Eclipsed **Staggered**

Newman projection

Condition for Optical activity

Presence of chirality (asymmetry) is essential condition for optical activity means the molecule must be chiral (It should not have any symmetry element).

Chiral Molecule

Optically active molecule. (Non-superimposable mirror images)

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Symmetry Elements

Presence or absence of chiral carbon not a necessary condition for optical activity.

The necessary condition for optical activity is absence of elements of symmetry.

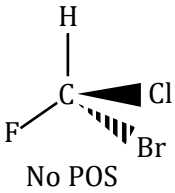
The elements of symmetry are

(a) Plane of symmetry (POS)

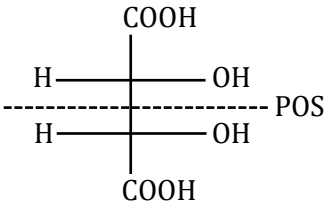
(b) Centre of symmetry (COS)

(a) Plane of symmetry (POS)

A plane which divides molecule in two equal halves is known as plane of symmetry.

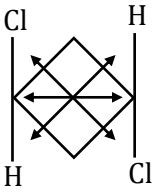


No POS



(b) Centre of symmetry (COS)

It is an imaginary point in the centre of a molecule such that if a line is drawn from any group of the molecule to this point and then extended to an equal distance beyond the point, it meets the mirror images of the original group.



Types of Configuration

1. R-S configuration (Absolute configuration)
2. D-L configuration (Relative configuration)
3. Erythro and Threo

1. R-S configuration (Absolute configuration):

R = Rectus (clockwise rotation)

S = Sinister (anticlockwise rotation)

(a) R-S configuration in Fischer Projection

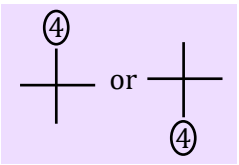
Rule I - Priority between the different groups attached on chiral carbon is determined by CIP rules.

Rule II- When 4th priority group is present at vertical line of Fischer projection, then we move

$1 \rightarrow 2 \rightarrow 3$

If clockwise (↷) R

Anti-clockwise (↶) S



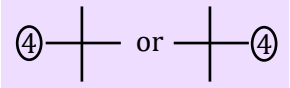
Rule III - When 4th priority group is present at horizontal line of Fischer projection.

Now,

$1 \rightarrow 2 \rightarrow 3$

If clockwise (↷) S

Anti-clockwise (↶) R



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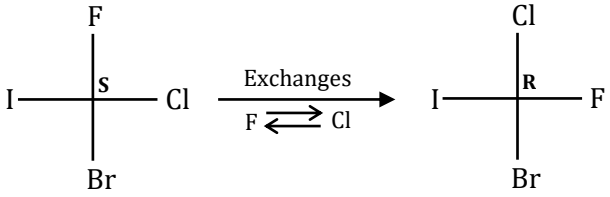
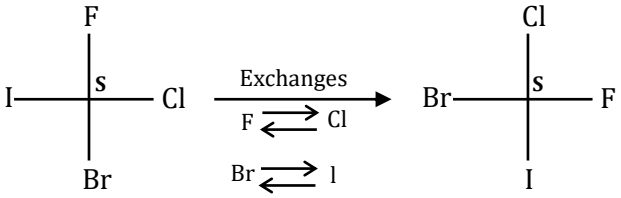
Rule of odd/even interchange

- When any two groups around a chiral carbon are exchanged, then configuration of molecule get reversed.

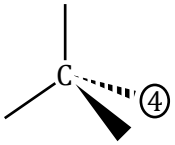


- When any two groups around a chiral carbon are exchanged even number of times, then configuration of molecule remains same.



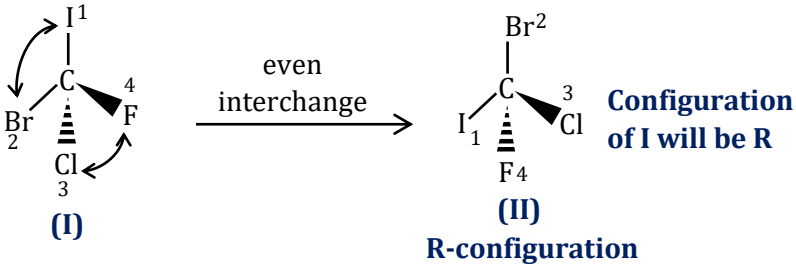
(b) R-S configuration in wedge dash

Rule I – When 4th priority group is on dash.



go 1→2→3
If clockwise (↷) R
anti-clockwise (↶) S

Rule II - If 4th priority is not on dash position then by even interchange 4th priority is taken on dash position and then find R-S configuration.



(I)

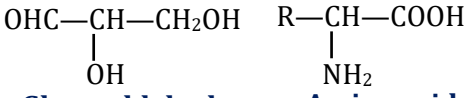
(II)

Configuration of I will be R

R-configuration

2. D-L configuration (Relative configuration):

- D or L is applied for amino acids and carbohydrates.
- The basic unit for D-L configuration is glyceraldehyde and α-Amino acid.



Glyceraldehyde **α-Amino acid**

Rules for D-L configuration :-

(a) Most oxidised group should be present at the top of vertical line in Fischer projection.

(b) $-CH_2OH$ or -R should be present at the bottom of vertical line in Fischer projection.

(c) At last chiral center, the relative position of –OH in carbohydrates and $-NH_2$ in amino acid defines D-L i.e. right side = D and left side = L.

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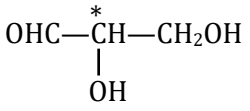
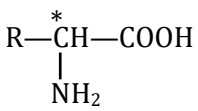
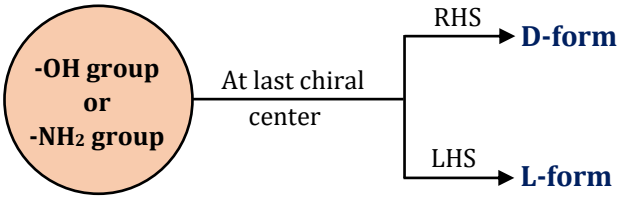
Example:



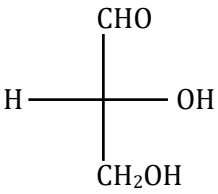
Glyceraldehyde



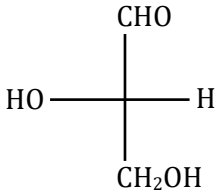
α-Amino acid



(1)

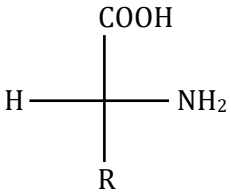


D-Glyceraldehyde

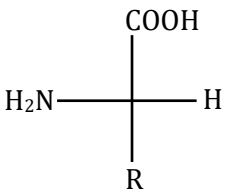


L-Glyceraldehyde

(2)



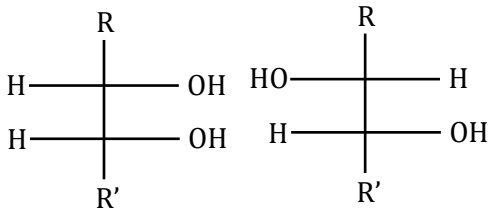
D-Amino acid



L-Amino acid

3. Erythro and Threo:

If same groups comes on the same side on two horizontal lines, then it is called erythro.
If same groups comes on the opposite side on two horizontal lines, then it is called threo.



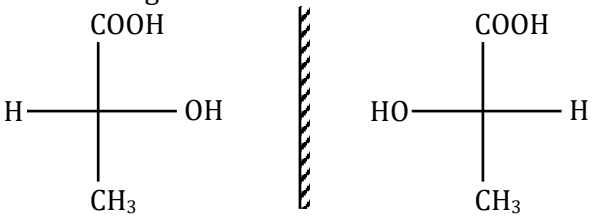
Erythro

Threo

Note : Erythro and threo are pair of diastereomers.

Enantiomers

(i) Some stereoisomers are mirror images of each other but do not superimpose on each other. Non-superimposable mirror images are called as enantiomers.



Object (I) mirror Object (II)

I and II are non-superimposable mirror images, so I and II are enantiomers.

(ii) Enantiomers are optically active substances. They rotate the plane polarized light in opposite directions but to the equal extent.

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Diastereomers

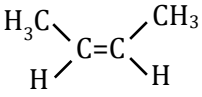
(i) Stereoisomers which are not mirror image of one another.

(ii) They have different physical and chemical properties and hence can be separated by fractional distillation, etc.

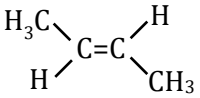
(iii) May or may not be optically active.

(iv) Geometrical isomers are also diastereomers of each other. (not mirror images)

1. But-2-ene



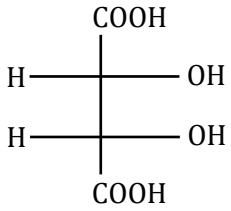
cis-But-2-ene



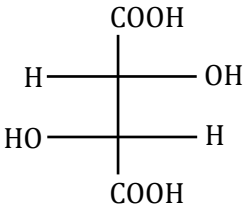
trans-But-2-ene

Illustration 1:

(1)

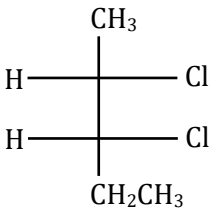


(2)

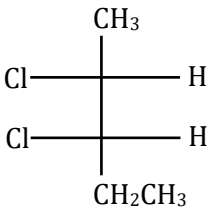


Solution: (1) and (2) are diastereomers.

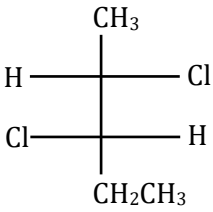
Illustration 2:



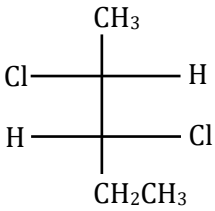
(I)



(II)



(III)

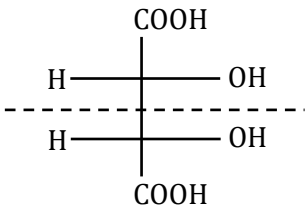


(IV)

Solution: I, II = Enantiomers, III, IV = Enantiomers
I, III = Diastereomers, II, IV = Diastereomers
II, III = Diastereomers, I, IV = Diastereomers

Meso compounds

Compounds having atleast two chiral carbons and element of symmetry is called meso compounds. It is optically inactive due to internal compensation.



Plane of symmetry

(achiral molecule, optically inactive)

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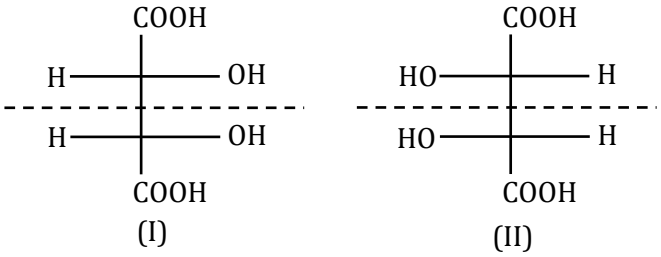
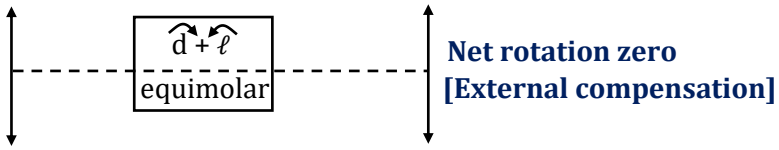
Illustration 3:



Solution: I and II are identical (mirror image of meso compound is identical)

Racemic mixture

Equimolar mixture of d and ℓ enantiomers is called as racemic mixture. (dℓ or (±)).



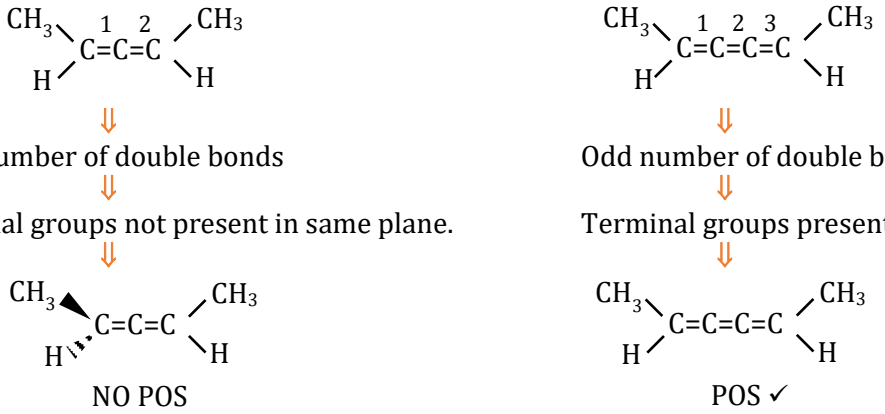
"Racemic mixture is optically inactive due to external compensation.

Special cases

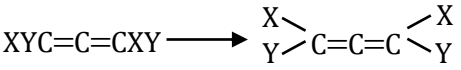
Presence or absence of chiral center is not a necessary condition for optical activity. The necessary condition is absence of element of symmetry.

1. Substituted Allenes:

Substituted allenes (cumulenes)



- Substituted allenes do not have chiral carbons but molecule is chiral, so show optical isomerism.

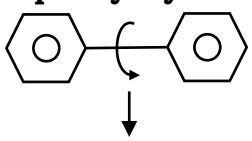


Allene

Optically active

Only those substituted allenes will be optically active in which "each sp^2 carbon have different atoms or group" and even number of double bonds present in it.

2. Biphenyl system:



Free rotation possible (optically inactive)

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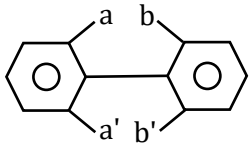
Ortho ortho' substituted Biphenyl

If all four ortho positions are occupied by bulky groups, then to minimise repulsion rings become perpendicular to each other.

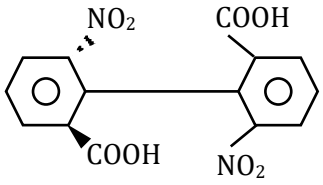


Bulky groups: –R, –Cl, –Br, –I, –CHO, –COOH, –COOR, $–CONH_2$, $–SO_3H$, $-NR_2$ etc.

Condition for O.I.

$a \neq a'$ and $b \neq b'$, optical isomerism is possible.

They do not have any chiral carbon but they are optically active.



Horizontal Plane **Vertical Plane**

Number of stereoisomers

Calculation of Optical Isomers: (Optically active + optically inactive)

S.N.	Nature of compounds	No. of optically active isomers (a)	No. of meso compounds (m)	Total no. of optical isomers (a + m)
1	**Compounds having more than one chiral centre with dissimilar ends.**	2^n (n = No. of chiral centre)	0	(2^n+0)
2	**Compounds having even number of chiral centres with similar ends**	2^{n-1}	$2^{\frac{n}{2}-1}$	$2^{n-1}+2^{\frac{n}{2}-1}$
3	**Compounds having odd number of chiral centres with similar ends**	$2^{n-1}-2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$	2^{n-1}

Total number of stereo isomer (TSI):

(A) If molecule is unsymmetrical

T.S.I. = 2^n

where n = No. of G.I. sites + O.I. sites

(B) If molecule is symmetrical

T.S.I. = $\boxed{2^{n-1}+2^{p-1}}$

- n = odd $\Rightarrow p=\frac{n+1}{2}$
- n = even $\Rightarrow p=\frac{n}{2}$

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(C) In case of ring system when G.I. center and O.I. center same then Stereoisomers = Optical isomers

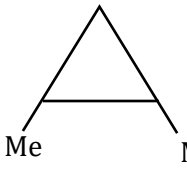
Ex.  ⇒ S.I. = O.I.

Illustration 4: $CH_3—\underset{\underset{OH}{|}}{CH}—\underset{\underset{Cl}{|}}{CH}—\underset{\underset{Br}{|}}{CH}—CH_3$

Solution: no. of optically active isomers = 8
no. of meso = 0
total no. of optical isomers = 8
no. of racemic mixtures =4 (Total active/2)

Illustration 5: $CH_3—\underset{\underset{OH}{|}}{CH}—\underset{\underset{OH}{|}}{CH}—CH_3$

Solution: no. of optically active isomers = 2
no. of meso = 1
total no. of optical isomers = 3
no. of racemic mixtures =1

BEGINNER'S BOX-1

1. Calculate total number of optical isomers in following compound :-

$CH_3—\underset{\underset{OH}{|}}{CH}—\underset{\underset{OH}{|}}{CH}—\underset{\underset{OH}{|}}{CH}—CH_3$

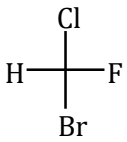
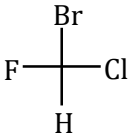
(1) 4 (2) 3 (3) 2 (4) 1

2. The simplest alkanol exhibiting optical activity is

(1) n-butyl alcohol (2) Isobutyl alcohol (3) s-butyl alcohol (4) t-butyl alcohol

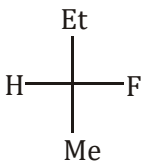
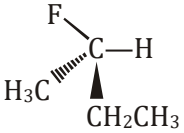
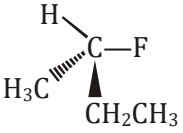
3. Which is optically active molecule :-

(1) $C_6H_5—\underset{\underset{O}{\|}}{C}—OH$ (2) $CH_3—\underset{\underset{OH}{|}}{CH}—C_2H_5$ (3) $C_6H_5—\underset{\underset{H}{|}}{CH}—OH$ (4) $C_6H_5—\underset{\underset{CH_3}{|}}{CH}—CH_3$

4. The following two compounds  and  are

(1) Enantiomers (2) Diastereomers (3) Identical (4) Epimers

5. Which of the following has 'S' configuration :-

(1)  (2)  (3)  (4)

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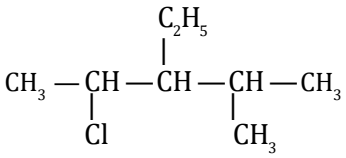
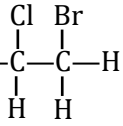
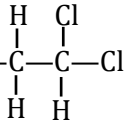
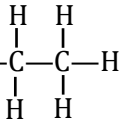
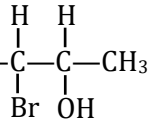
BEGINNER'S BOX-2

1. How many chiral carbon atoms are present in following molecule ?



(1) 1 (2) 2 (3) 3 (4) 4

2. Which one of the following contains asymmetric carbon atom?

(1)  (2)  (3)  (4) 

3. An organic compound exhibits optical isomerism when

(1) Four groups linked to carbon atom are different

(2) Three groups linked to carbon atom are different

(3) Two groups linked to carbon atom are different

(4) All the groups linked to carbon atom are same

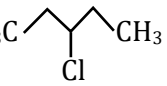
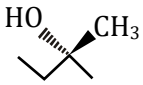
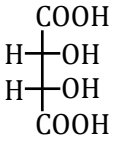
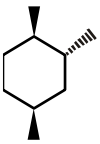
4. Rotation of plane polarised light is measured by

(1) Manometer (2) Polarimeter (3) Viscometer (4) Refractometer

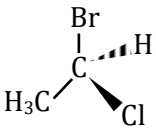
5. Which of the following compounds is not chiral?

(1) $DCH_2CH_2CH_2Cl$ (2) CH_3CH_2CHDCl (3) $CH_3CHDCH_2CH_2Cl$ (4) $CH_3CHClCH_2D$

6. Which is optically active?

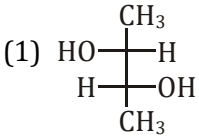
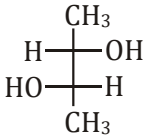
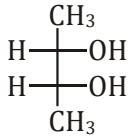
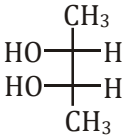
(1)  (2)  (3)  (4) 

7. The configuration of the compound

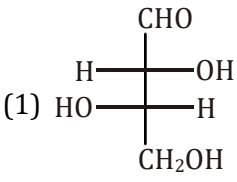
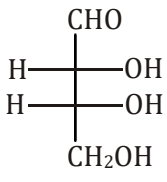
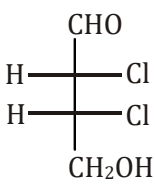


(1) R (2) S (3) Z (4) E

8. (2R,3R)-2,3-Butanediol is:-

(1)  (2)  (3)  (4) 

9. Which of the following compounds is Erythro?

(1)  (2)  (3)  (4) Both 2 and 3

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10. Which of the following can show enantiomerism?

(1) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

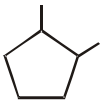
(2) $CH_2=CHCH_2CH_2CH_3$

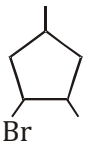
(3) $CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$

(4) $CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$

11. Which of the following can be a meso compound?

(1)

(2) 

(3) 

(4) All of these

BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1						
	Que.	1	2	3	4	5
	Ans.	1	3	2	1	3

BEGINNER'S BOX-2										
	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	2	4	1	2	1	4	1	1	4	4
	Que.	11									
	Ans.	2									

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